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S.T. Weir
J. Akella
Y.K. Vohra
S.A. Catledge

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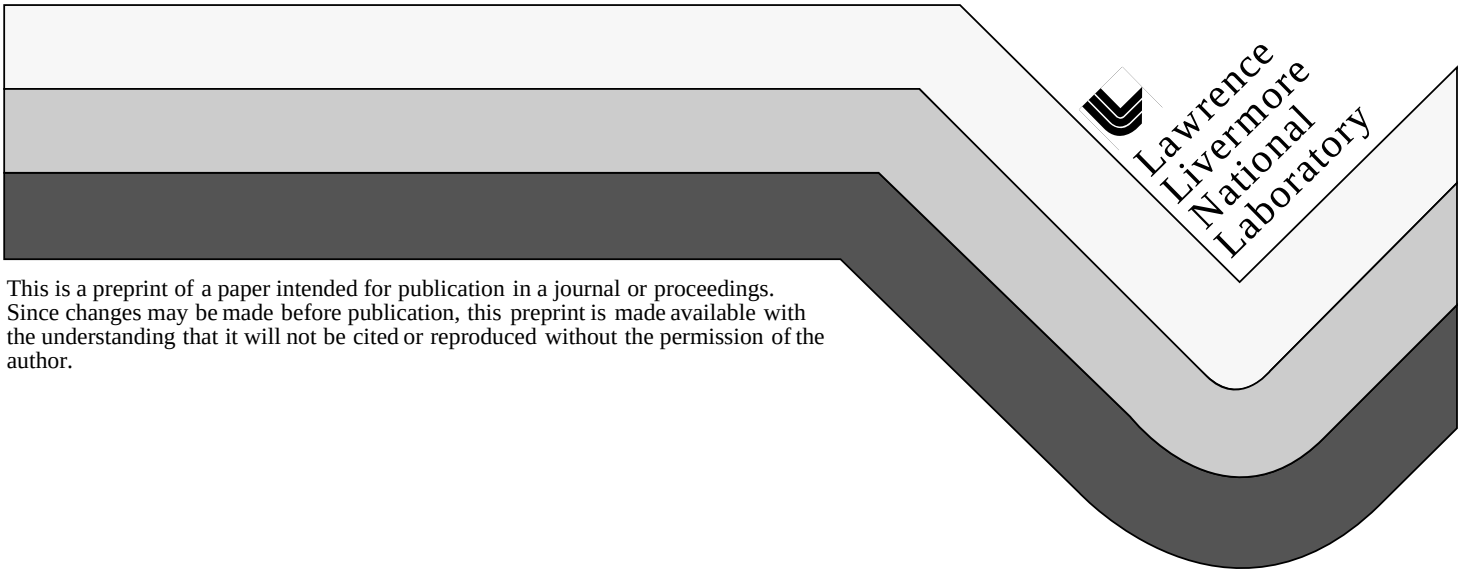

Diamond Anvils with Integrated Diamond-Encapsulated Microprobes for High-Pressure Electrical Transport Experiments

S.T. Weir*, J. Akella*, Y.K. Vohra †, and S.A. Catledge†
* *Lawrence Livermore National Laboratory, University of California, Livermore, CA 94550 USA*
† *Department of Physics, University of Alabama at Birmingham, Birmingham, AL 35294 USA*

We have fabricated diamond anvils specially designed for use in ultra-high pressure electrical transport experiments. These anvils, which we refer to as "designer anvils", feature thin-film metal microprobes which are encased in a layer of high-quality, epitaxial, chemically vapor deposited (CVD) diamond. The synthetic diamond film ensures that the microprobes are survivable to Mbar pressures, and also serves to electrically insulate the microprobes from the high-pressure gasket. High-pressure resistivity experiments were performed on KI and FeO to pressures of approximately 1.8 and 1.7 Mbars, respectively. Future possible applications of designer anvils are also discussed.
[electrical conductivity, synthetic diamond, band overlap, metallization, designer anvils]

1. Introduction.

Electrical transport experiments are among the most difficult and challenging of ultra-high pressure experiments with diamond anvil cells (DAC's). Although electrical conductivity experiments have recently started to be performed at Mbar pressures [1,2], these experiments require very careful and painstaking preparation. Standard high-pressure electrical transport techniques involve the use of thin metal wires or foils which must be carefully maneuvered into place on top of a small sample in a specially prepared alumina gasket, which makes precise placement of the probes problematic. In addition, due to the very large amount of plastic flow of the gasket which accompanies the pressurization of the sample, electrical contact to the sample may be lost, or the wires or foils may short-circuit to each other or to the surrounding metal gasket. All of these difficulties have limited the maximum pressures to which electrical transport experiments can be performed, as well as the precision with which the measurements can be made. These difficulties have also limited the number of ultra-high pressure techniques which can be performed at ultra-high pressures. For example, at the present time, no NMR, Hall effect, or internal ohmic heating experiments have yet been performed at Mbar pressures.

The goal of our project is to free high-pressure electrical transport experiments from these bounds and limitations by making use of recent advances in epitaxial, CVD diamond deposition technology and advanced lithography techniques to fabricate custom-designed diamond anvils specially suited for electrical transport experiments at Mbar pressures. We refer to these custom-designed diamond anvils as "Designer Anvils".

2. "Designer Anvils"

A. Designer Anvil Fabrication

Two key concerns with present electrical transport techniques are (1) a lack of wire layout precision and (2) a lack of mechanical robustness in the wire layout, as well as in the surrounding electrical insulation. We have addressed these concerns by fabricating special diamond anvils in which Mbar-survivable electrical leads are an integrated part of the anvil design.

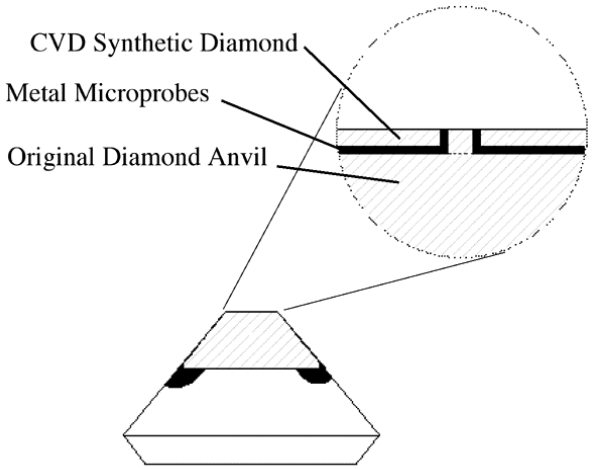

Figure 1. Schematic diagram of a designer anvil for electrical transport experiments.

Figure 1 shows a schematic diagram of a diamond anvil intended for electrical conductivity experiments. A thin-film metal electrode pattern was fabricated on the surface of a standard, 1/3-carat diamond anvil using optical lithography with a Canon projection 4:1 aligner machine. The electrode pattern consists of four thin-film metal probes (0.5 μm thick; 10 μm wide) which are exposed at the center of the diamond culet, and extend down the sides of the anvil to exposed side pads. For electrical insulation, the electrodes are then encased in a layer of high-quality, homoepitaxial diamond film. The diamond is deposited by a microwave plasma chemical vapor deposition system (MPCVD). This system uses a 2% methane in hydrogen gas mixture and a substrate temperature of 1100 ˚C, with a typical chamber pressure of 90 Torr and an average microwave power of 850 W. Appreciable surface roughness exists in the as-grown diamond film, and so some repolishing is necessary before the anvil is ready to be used in a high-pressure experiment. A completed designer anvil is shown in Figure 2. The quality of the synthetic diamond film

is quite high, as evidenced by the high transparency of the film.

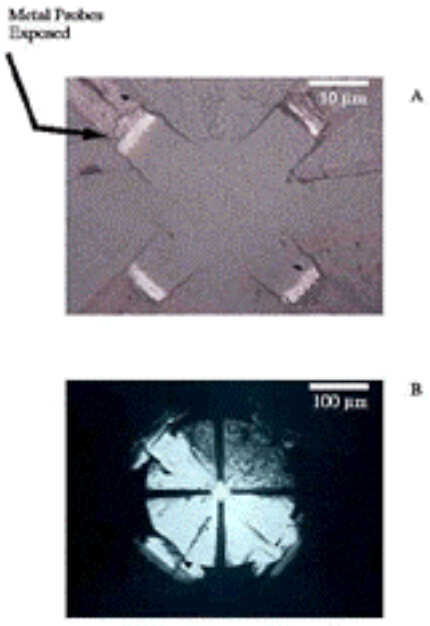

Figure 2. A completed designer anvil for high-pressure electrical transport experiments. (A) Magnified view of the center of the culet showing the exposed metal probes for making electrical contact to the sample. (B) View of the overall culet under backlighting conditions.

B. Diamond Film Characterization

The CVD diamond films are of high quality and show evidence of highly epitaxial growth. Figure 3 shows an as-grown film of CVD diamond on a diamond anvil culet. The square morphology of the growth structure is indicative of highly epitaxial growth of diamond onto the single crystal diamond anvil substrate, with the edges of the square growth structure aligned along the <100> directions. Microtwins and diamond growth steps are also evident in the as-grown surface. Photoluminescence and Raman spectroscopy experiments confirm the fact that the diamond film is of extremely high quality with a very small sp^2-carbon content. We have presented the results of an experiment testing the adhesion of this deposited film to the diamond anvil under actual high-pressure DAC stress conditions elsewhere [3].

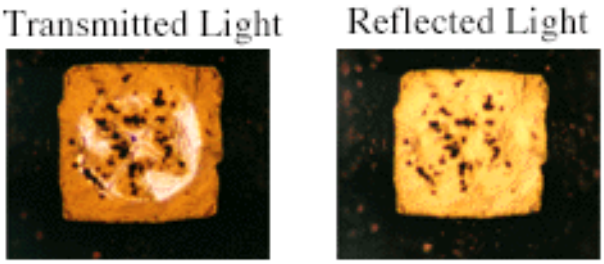

Figure 3. As-grown diamond film on the culet of a 300 μm diameter flat diamond anvil. The culet lies in the {100} plane, and the square growth morphology is indicative of high-quality epitaxial growth.

3. High-Pressure Electrical Conductivity Experiments

We have performed electrical conductivity experiments on two materials, KI and FeO, with our designer anvils. Both experiments were prepared by indenting a spring steel gasket and then drilling out the entire culet of the indented region with an electrical discharge machine (EDM). Alumina powder was then packed into the gasket region, and a slight depression was made in the powder to accommodate the sample. A small sample of KI or FeO was placed into this depression, along with small ruby chips to serve as pressure markers. The sample pressure was either determined by ruby fluorescence measurements, or by x-ray diffraction from either the sample itself or from alumina, with the known P-V equation-of-state (EOS) of either the sample or alumina being used to calculate the pressure.

A. Potassium Iodide (KI)

KI is expected to metallize at pressures somewhat above 1 Mbar by a band-overlap, insulator-to-metal (IM) transition. At ambient pressure, it crystallizes in the B1 (NaCl) structure, with an electronic band gap of 6.0 eV. At a pressure of 1.9 GPa, it transforms to the B2 (CsCl) structure, and remains in this structure to at least 70 GPa [4]. Our stoichiometric sample was obtained from Johnson-Matthey and rated to be 99.999% pure.

Optical absorption experiments [4] examining the band edge absorption threshold in KI indicate that the band gap should close to zero at approximately V/V_o=0.36 which, according to the EOS of Asaumi *et. al* [4], corresponds to a pressure of 115 GPa. Band structure calculations by Amirthakumari, *et al.* [5] using a semi-relativistic tight-binding linear muffin tin orbital (TBLMTO) method predict band overlap at V/V_o =0.350 or P=125.8 GPa. Finally, the Herzfeld criterion of

$$\frac{V_m}{V_o} = \frac{n^2 - 1}{n^2 + 2} \qquad \text{(Eqn. \#1)}$$

where V_m is the metallization volume and *n* is the ambient pressure index of refraction (n=1.677), gives $V/V_o = 0.376$ (P=98.2 GPa).

A plot of resistance vs. pressure for KI is given in Figure 4. These measurements were two-probe measurements in which the residual probe resistance of 40-80 ohms was subtracted from the total overall resistance measurement to give the sample resistance. Below 80 GPa, the resistance of the sample was too high to be measurable. But above 80 GPa, we were able to measure a resistance which dropped exponentially with increasing pressure. The resistance eventually dropped to a minimum resistance of about 100 Ω at pressures above 140 GPa, and remained at this value out to the highest pressure reached in this experiment of 175 GPa. From the resistance vs. pressure behavior, we identify the metallization pressure to be 131 GPa, based on the intersection of the fitting lines shown in Figure 4. The sample at this pressure is quite reflective and shiny under reflected light, although it has a brownish tinge when viewed under transmitted light. This appearance is consistent with a metal having a low density of charge carriers, as might be expected for a material which has just undergone band-overlap metallization.

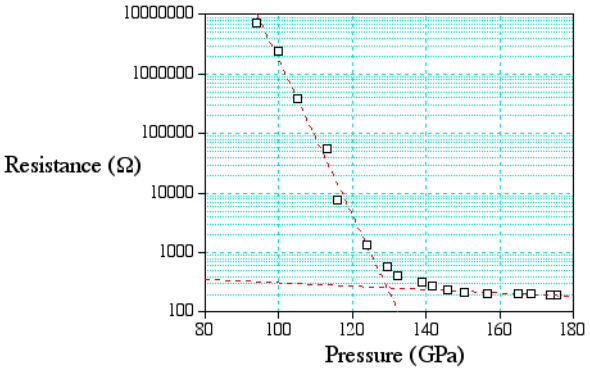

Figure 4. Resistance vs. Pressure for Potassium Iodide (KI)

B. Iron-Oxide (FeO)

FeO is non-metallic at ambient pressure, but is predicted to metallize by a band-overlap I-M transition at Mbar pressures. It has a somewhat reflective appearance at ambient pressure and an electrical resistivity of about 0.2 Ω-cm. High-pressure electrical conductivity experiments by Knittle and Jeanloz [6] to 80 GPa on $Fe_{0.97}O$ reveal that the resistivity drops only very slowly with increasing pressure, the drop in resistivity being less than an order of magnitude as the pressure increases from zero to 80 GPa. These results are not expected to be sensitive to stoichiometry. Our sample was obtained from Sigma-Aldrich and had a stated chemical purity of 99.9%, and an Fe to O ratio within 0.5% of stoichiometry.

A plot of resistance vs. pressure for FeO to 120 GPa based on ruby pressure calibration is shown in Figure 5. Consistent with the data of Knittle and Jeanloz [6], we find that the general trend is for the resistance to slowly drop with increasing pressure. We observe, however, slight fluctuations or oscillations in the resistance vs. pressure behavior which apparently were not observed by Knittle and Jeanloz. It is uncertain at this point whether these oscillations do in fact reflect variations in the sample resistivity, or whether small creep effects in the alumina gasket might be causing the resistances to vary. More experiments will be needed to examine this behavior further. Additional data was taken at pressures up approximately 170 GPa, with pressure calibration based on x-ray diffraction from the alumina in the vicinity of the sample. However, no sharp drop in resistance was found even under pressures to approximately 170 GPa, which suggests that FeO has not yet metallized.

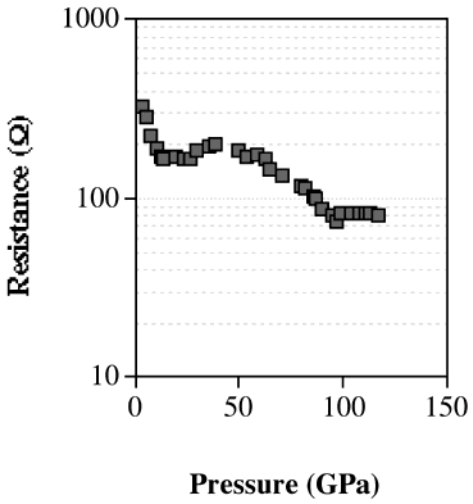

Figure 5. Resistance vs. Pressure for FeO.

4. Discussion

In these first two Mbar electrical resistivity experiments using designer anvils, we have studied KI and FeO. The KI data shows clear evidence of a band-overlap insulator-to-metal transition, with metallization occurring at 131 GPa. This pressure is considerably higher than that based on the Herzfeld criterion (P=98.2 GPa), but very close to the metallization pressure of 125.8 GPa predicted on the basis of band structure calculations [5]. For comparison, recent high-pressure conductivity experiments on the alkali-halide CsI found its metallization pressure to be 115 GPa [1], which is somewhat below the metallization pressure of KI (131 GPa).

FeO shows much different behavior. Consistent with earlier high-pressure conductivity experiments [6], we find

that the electrical resistivity tends to drop very slowly with increasing pressure, and that the signal shows no evidence of metallization even at the highest pressure of approximately 170 GPa. Indeed, band-structure calculations by Sherman and Jansen [7] indicate that FeO should not metallize due to band closure at any pressure below 200 GPa (at room temperatures). The metallization of FeO in the high-pressure and -temperature B8 structure (NiAs structure) is believed to result from itinerant 3d electrons rather than from a band closure of the Fe(3d)-O(2p) gap.

These first Mbar electrical conductivity experiments with designer anvils demonstrate that designer anvil technology has reached the stage where rapid future advances can be expected. Designer anvils are mechanically robust under Mbar pressures and feature microprobe patterns which can be fabricated with a high degree of precision. In addition to high-pressure electrical conductivity experiments, future high-pressure applications of this technology include ultra-high pressure NMR experiments, Hall effect experiments, and high-pressure and -temperature experiments using internal resistive heating.

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